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ORIGINAL ARTICLE

Gold nanoparticles, capped by carboxy-calix[4]resorcinarenes: effect of structure and concentration of macrocycles on the nanoparticles size and aggregation

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Abstract

Small ($d_{core} \approx 2$–5 nm) well-dispersed gold nanoparticles (AuNPs) stabilized by amphiphilic octacarboxy-calix[4]resorcinarenes with different substituents on the lower rim—methyl (**C_1–CR**), pentyl (**C_5–CR**) and undecyl (**C_{11}–CR**)—in an aqueous solution were obtained. The nanoparticles were studied by spectrophotometry, transmission electron microscopy, FTIR-spectroscopy, dynamic light scattering, small angle X-ray scattering and X-ray powder diffraction. The influence of $HAuCl_4$/macrocycle ratio during the synthesis on the nanoparticles size and aggregation only for weakly associated **C_1–CR** and **C_5–CR** was achieved. The self-association effect of **C_{11}–CR** on the nanoparticles stabilization is found. The existence of gold in the form of crystallites and their average sizes were defined. The average nanoparticle sizes were determined and the structure of macrocyclic shells on the surface of nanoparticles in an aqueous solution was proposed. The formation of cooperative calix[4]resorcinarene associates on the AuNPs surface due to the multiple supramolecular interactions leads to the creation of functional gold nanoparticles.

Keywords Calixresorcinarene · Macrocycle · Gold nanoparticles · Self-association · Supramolecular aggregates

Introduction

Recently, gold nanoparticles (AuNPs) have captured the great attention and are very popular among the researchers because they have incomparable optical and electronic properties due to the presence of localized surface plasmon resonance (SPR) [1, 2]. This unique property makes possible using of AuNPs in the field of biomedicine and drug delivery [3], catalysis [4] and sensing [5]. It is known that size and shape of AuNPs and also their ability to aggregate influence on the value of the gold SPR intensity. Thus, controlling the physical characteristics of the AuNPs the ability to influence on their physico-chemical properties is appeared, which is a necessary condition for the creation of new nanoscale systems.

A lot of well-known methods are used to synthesize AuNPs [6–8], but the stabilization of obtained nanoparticles is great functional moment in the sphere of directed nanomaterial creation, since it allows forming nanoparticles in a suitable form or size range for each challenge [9, 10]. For such an important process of nanoparticles stabilization, various organic modifying compounds containing carboxylic [6, 7, 11], amine [12], thiol [13], phosphine [14] and other functional groups which are capable of binding with the surface of AuNPs and the formation of stable and monodisperse colloids are known.

However, the challenge of the synthesis of AuNPs, modified by compounds, using of which leads to the production of new materials and structures that have unique biocompatible receptor [15, 16], catalytic [17], photoactive or sensor [18]

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